

## Covalently Immobilized Polyethylenimine for CO<sub>2</sub> Adsorption

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### Electronic Supporting Information

#### Material Preparation

Aluminosilica was prepared as follows: 4 g of TMAOH was diluted with water (38.5 g) before adding 5.7 g CTAB under vigorous stirring. After 15 min, 0.2 g of NaAlO<sub>2</sub> was added and stirring continued for 30 min, after which 2.1 g Cab-O-Sil was added. The composition of the synthesis mixture was 1.0 SiO<sub>2</sub>:0.317 TMAOH:0.45 CTAB:0.035 Al<sub>2</sub>O<sub>3</sub>:67 H<sub>2</sub>O, with a nominal Si/Al ratio of ca. 15. The mixture was then sealed in an autoclave and placed in an oven preheated at 80 °C for 40 h. The obtained material was filtered, washed extensively and dried under ambient conditions to afford as-synthesized aluminosilica. Partial surfactant (CTAB) extraction was carried out in EtOH and room temperature. Pore expansion was carried out through hydrothermal treatment of the resultant dried powder in the presence of DMDA. To a mixture of DMDA (1 g) and water (30 g) at RT, 0.8 g of the as-synthesized sample was added. After stirring for an hour, the mixture was heated at 120 °C for 2 days under autogenous pressure. The solid material was collected by filtration, dried at ambient temperature and calcined in flowing N<sub>2</sub> at 550 °C by raising the temperature at 1 °C/min. The gas was then switched to air at 550 °C and kept for 5 h to remove any remaining carbonaceous material, to afford PE- $\text{AlSiO}_2$ .

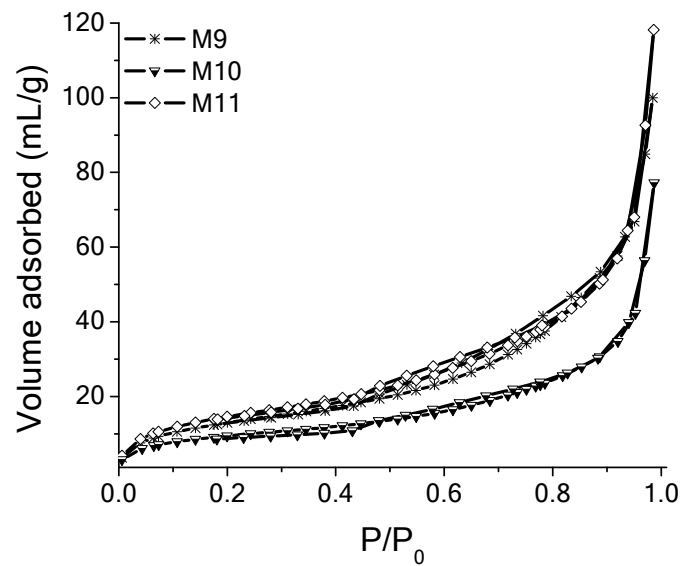
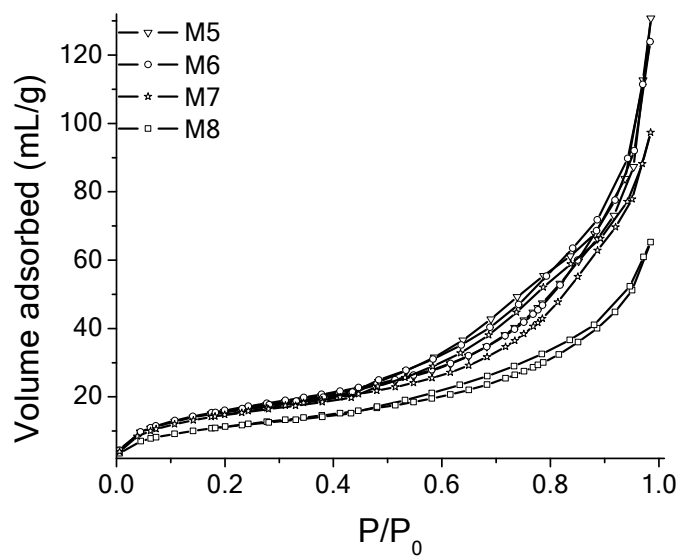
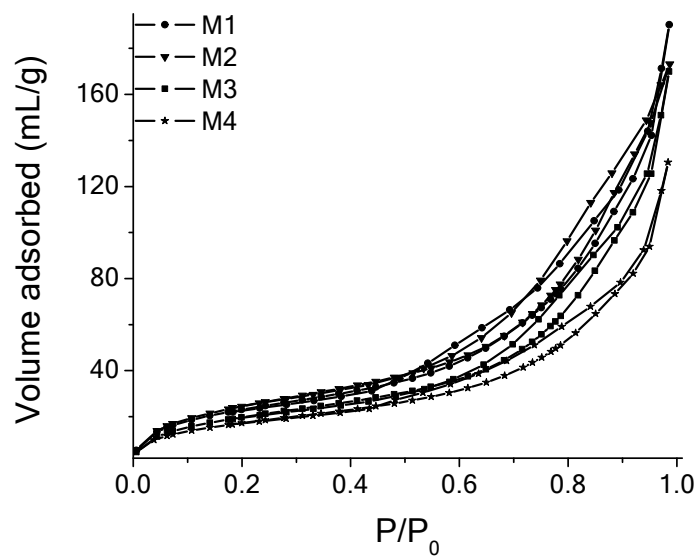
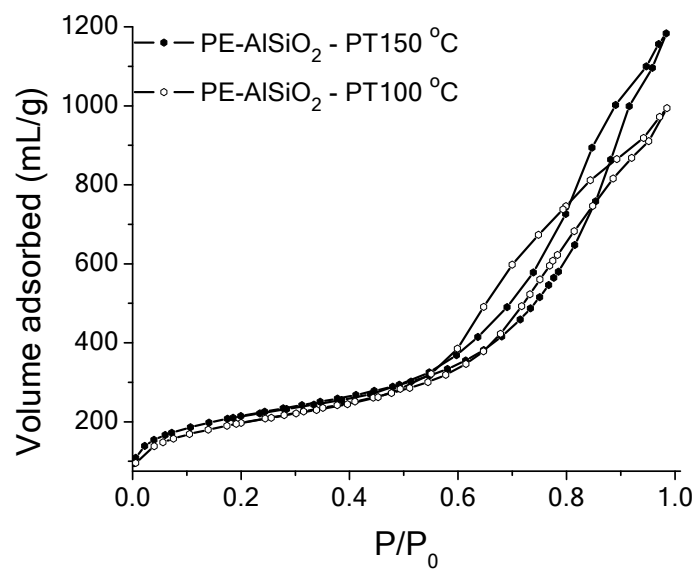


Figure S1. Nitrogen adsorption–desorption isotherms of pristine and functionalized supports.

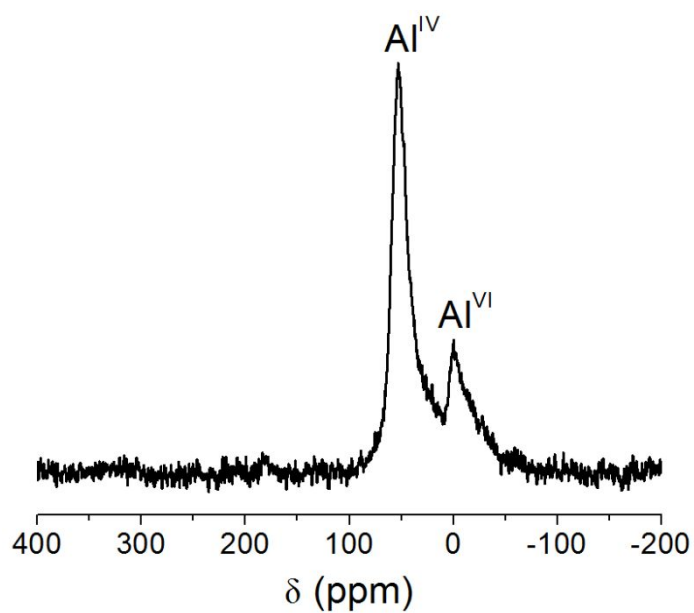


Figure S2.  $^{27}\text{Al}$  NMR spectra of PE-AlSiO<sub>2</sub>

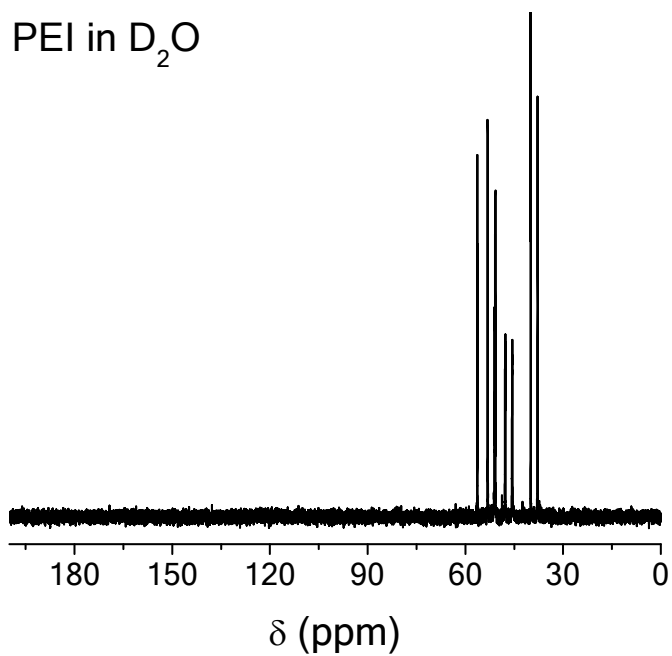


Figure S3.  $^{13}\text{C}$  NMR spectra of PEI in D<sub>2</sub>O

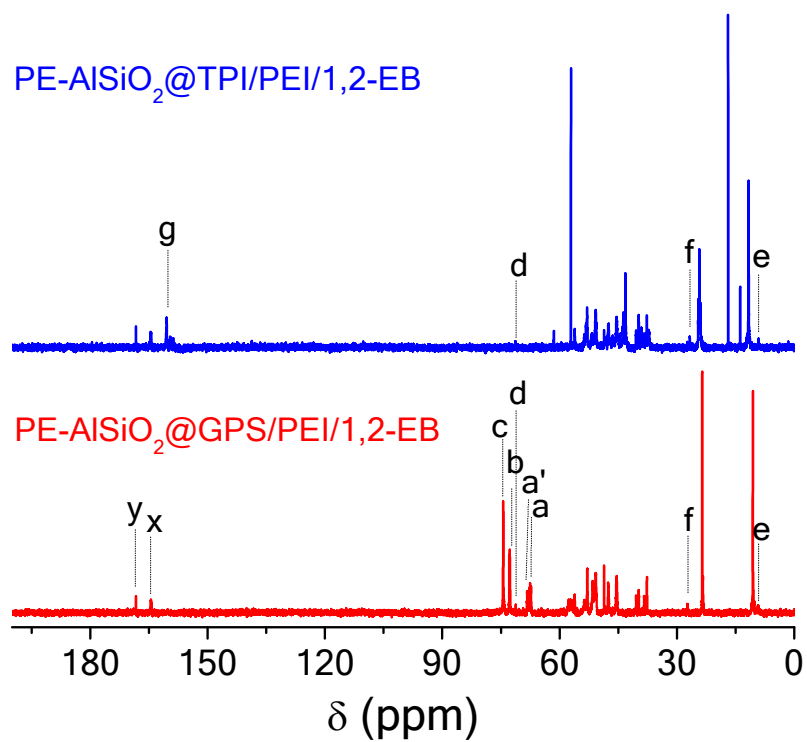


Figure S4.  $^{13}\text{C}$  NMR of solid materials, with higher grafting agent-to-PEI ratio, dissolved in 10% NaOH ( $\text{D}_2\text{O}$ ).

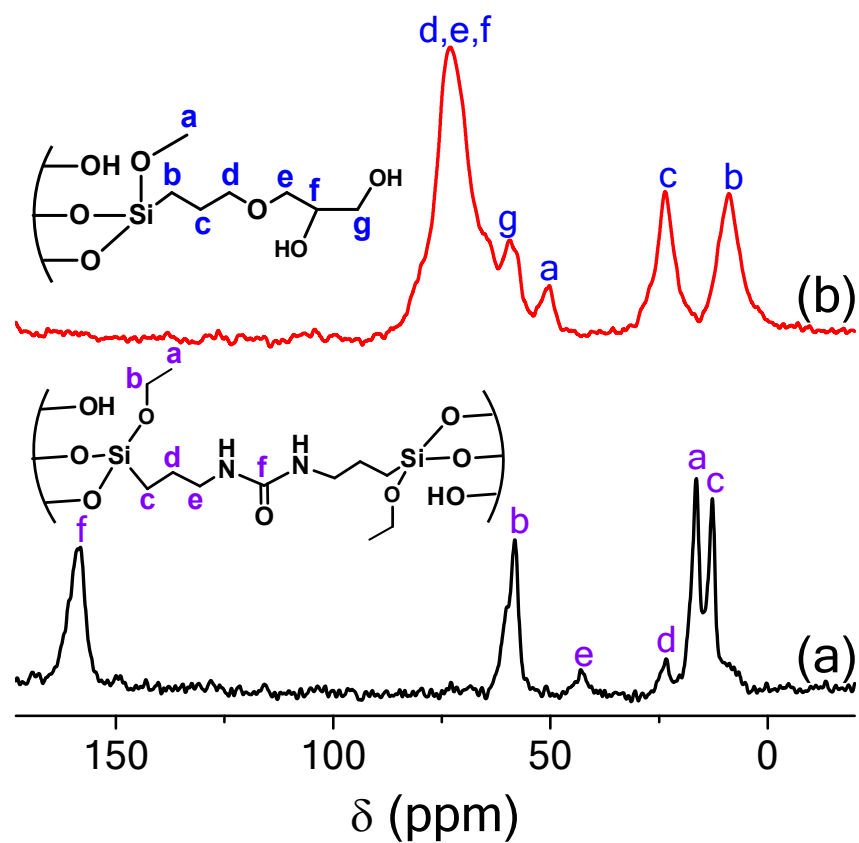
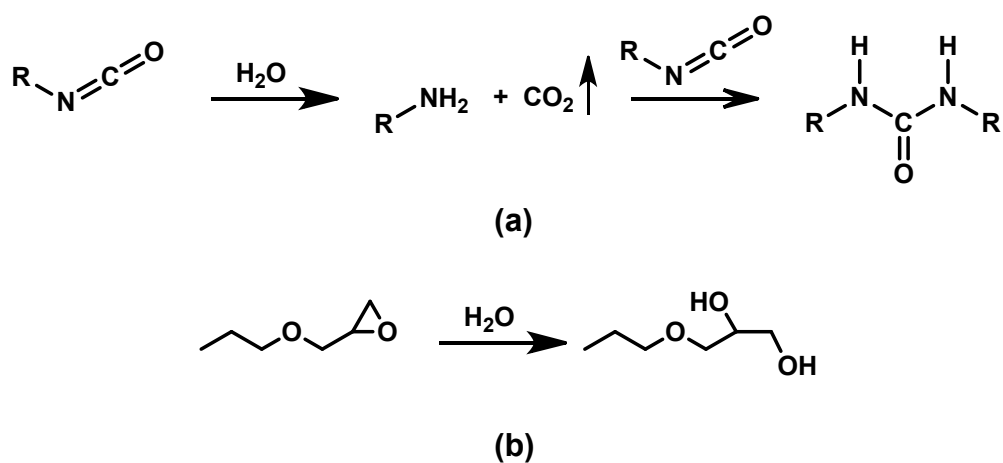


Figure S5.  $^{13}\text{C}$  CP-MAS NMR spectra of GPS (top) and TPI (bottom) immobilized on PE- $\text{AlSiO}_2$  in anhydrous toluene



Scheme S1. Reaction of (a) isocyanate and (b) 2-(propoxymethyl)oxirane with water to form urea and diol, respectively

Table S1. Changes in CO<sub>2</sub> capacity and organic content following leaching in EtOH

Entry	Material	CO <sub>2</sub> uptake (mmol/g)			Organic content (wt%)		
		Fresh	EtOH-leached	% difference	Fresh	EtOH-leached	% difference
1	M1 - 68	2.76	0.48	83	47.18	23.63	50
2	M2	2.76	1.17	58	52.32	30.39	42
3	M3 - 59	2.89	1.34	54	47.31	32.07	32
4	M4	2.31	1.51	35	49.79	40.46	19
5	M5	2.28	1.39	39	49.82	38.78	22
6	M6	2.34	1.68	28	51.20	43.73	15
7	M7	2.46	1.83	26	51.58	45.59	12
8	M8	2.44	2.01	18	53.44	49.5	7
9	M9	2.19	1.56	29	49.15	45.24	8
10	M10	2.19	1.65	25	50.12	45.61	9
11	M11 - 62	2.75	1.15	59	51.64	36.47	29

Leaching test procedure: 0.5 g of material stirred in 50 mL EtOH for 2 h

Table S2. Variation of CO<sub>2</sub> uptake following thermal oxidation degradation at 100 °C over time

Entry	Material	Thermal oxidation duration			
		0 h	16 h	24 h	40 h
1	M1	2.76	-	0.63	-
2	M2	2.76	2.21	0.97	0.23
3	M7	2.46	1.84	1.05	0.34
4	M8	2.44	2.19	1.97	1.13
5	M9	2.19	1.95	1.55	0.76
6	M10	2.19	2.09	1.82	0.98
7	M11	2.75	-	1.05	-